FEATURE ARTICLE

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From group 13–group 13 donor–acceptor bonds to triple-decker cations

Alan H. Cowley

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas, 78712, USA. E-mail: cowley@mail.utexas.edu; Fax: (+1)512-471-6822; Tel: (+1)512-471-7484

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Donor–acceptor bonding between group 13 elements seems counter-intuitive because one normally thinks of *e.g.* boron and aluminium compounds as classical Lewis acids. Indeed, many such compounds have achieved industrial prominence in this regard. Recently, however, it has become possible to stabilize these and other group 13 elements in the +1 oxidation state as opposed to the archetypical +3 oxidation state. Moreover, it turns out that in the +1 oxidation state these species are excellent donors – hence the formation of these unprecedented donor–acceptor bonds. The discovery of such bonds has led, albeit indirectly, to the development of triple-decker main group cations. This aspect is also covered in the review.

Introduction

Trivalent organometallic compounds of the group 13 elements are normally thought of as Lewis acids. Classical examples of such acceptors include boron and aluminium trialkyls and triaryls.[1] The acceptor behaviour arises because of the presence of a formally vacant p-orbital and the absence of a lone pair of electrons on the group 13 element. However, Density Functional Theory (DFT) calculations on boranediyl and heavier univalent group 13 compounds, RM (R = Me, η^5-C_5Me_5, $(H_3Si)_2N$; M = B, Al, Ga, In) indicate that, regardless of the substituent, the ground state of each species is a singlet and that the singlet–triplet energy gap tends to increase with atomic number.[2] The HOMO's of the univalent RM molecules exhibit distinctly lone pair character as illustrated in Fig. 1 for four borane diyls. The HOMO's of the heavier congeners are qualitatively similar to those of the boranediyls; however, the "lone pair" contribution to the wave functions decreases with atomic number. In the cases of (η^5-C_5R_5)Ga and (η^5-C_5R_5)In, the HOMO is of e symmetry and corresponds to the π-bonds between the η^5-C_5R_5 fragment and the group 13 element. The nature of the LUMO's of the RM molecules is dependent upon the conjugative ability of the R substituent.

Alan H. Cowley was born in Manchester, UK. He attended the University of Manchester from 1952 until 1958, where he received BSc, MSc and PhD degrees. After a postdoctoral sojourn at the University of Florida, he returned to the UK in 1960 where he was employed as a research chemist by Imperial Chemical Industries until 1962. Most of his academic career has been spent at the University of Texas at Austin where he holds the Robert A. Welch Chair in Chemistry. He has close to 500 publications, most of which are concerned with synthetic, structural, and theoretical main group chemistry. He was elected a Fellow of the Royal Society in 1988 and received an Honorary Doctorate from the University of Bordeaux I in 2003. He has served on the Board of Trustees of the Gordon Research Conferences and on several Editorial Boards, including the Journal of the American Chemical Society, Inorganic Chemistry, and Organometallics.

The foregoing calculations brought us to the realization that the pentamethylcyclopentadienyl-substituted group 13 diyls should be able to function as Lewis bases and thus form group 13 donor–acceptor bonds with group 13 Lewis acids. The first example of a compound featuring an aluminium–boron donor–acceptor bond, (η^5-C_5Me_5)Al → $B(C_6F_5)_3$ (**1**)[3], was prepared by treatment of the aluminium tetramer, [Al(η^5-C_5Me_5)]$_4$[4] with $B(C_6F_5)_3$.[5] X-ray analysis of **1**[3] revealed that the C_5Me_5 ring is attached to aluminium in an η^5-fashion (Fig. 2) and that the ring centroid-Al–B angle is almost linear (172.9(1)°). Comparison of the average Al–C distance for **1** (2.171(3) Å) with those for the aluminium tetramer [Al(η^5-C_5Me_5)]$_4$ (2.344(13) Å)[6] and monomer (2.388(7) Å)[7] indicate that considerable shortening of the Al–C distances accompanies the formation of the Al → B donor–acceptor bond. Such a trend is anticipated because the transformation of the aluminium lone pair of (η^5-C_5Me_5)Al into the Al → B donor–acceptor linkage is expected to result in the development of partial positive and negative charges at aluminium and boron, respectively. The length

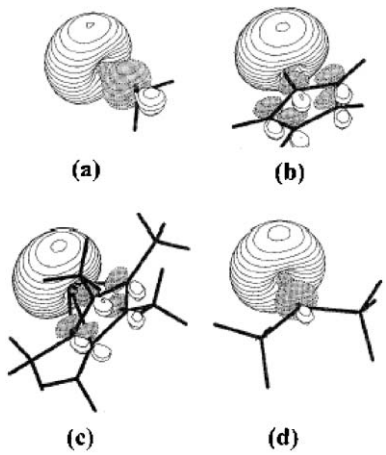

Fig. 1 Three-dimensional representations of RB "lone pair." View of the orbitals for (a) MeB, (b) (η^5-C_5H_5)B, (c) (η^5-C_5Me_5)B, (d) $(H_3Si)_2NB$.

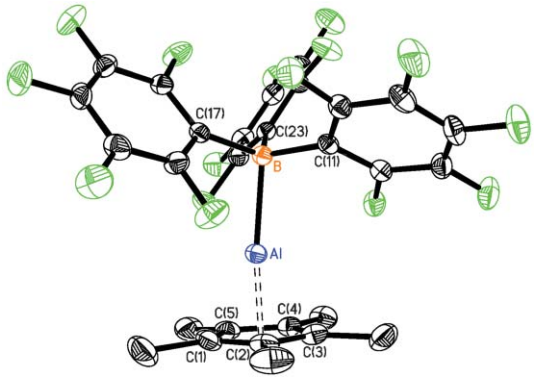

Fig. 2 View of the structure of (η^5-C_5Me_5)Al → $B(C_6F_5)_3$ (**1**).

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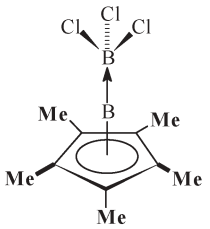
of the Al → B donor–acceptor bond is 2.169(3) Å. There are very little Al–B bond distance data in the literature with which to compare this value. The Al–B separations, in the hydride-bridged complexes, $Me_3NAl(\eta^2\text{-}H_2BH_2)_3$[8] and $[(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2]_2\text{-}Al(\eta^2\text{-}H_2BH_2)$[9] are 2.24(1) and 2.27(3) Å, respectively, while those in aluminium-substituted carboranes[10] range from ~2.13 to 2.24 Å. As a consequence of the donor action on the part of the alanediyl, the geometry of $B(C_6F_5)_3$ changes from trigonal planar to distorted tetrahedral as reflected by the sum of bond angles at boron [339.8(2)°]. As will be discussed in a subsequent section, the extent of this structural change can be taken as a measure of the Lewis basicity of the group 13 diyl.

Homonuclear dative bonds

DFT calculations[11] on the parent dialane, H_2AlAlH_2 indicate that this compound is more stable than the corresponding valence isomer HAl → AlH_3 by 9.17 kcal mol^{-1}. However, if one of the dialane hydride ligands is replaced by the π-donating cyclopentadienide ligand,[12] the valence isomeric structure $(\eta^5\text{-}C_5H_5)Al$ → AlH_3 becomes more stable than the dialane structure $(\eta^2\text{-}C_5H_5)(H)Al\text{–}AlH_2$ by 10.79 kcal mol^{-1}. The foregoing calculations suggested that it might be possible to prepare the first example of a compound with an aluminium–aluminium donor–acceptor bond by treatment of $[Al(\eta^5\text{-}C_5Me_5)]_4$ with the strong Lewis acid $Al(C_6F_5)_3\cdot PhCH_3$.[13] Indeed, this is the case.[11] The X-ray crystal structure of $(\eta^5\text{-}C_5Me_5)Al$ → $Al(C_6F_5)_3$ (**2**) bears a close resemblance to that of **1**. Thus, the C_5Me_5 ring is η^5-bonded to the donor aluminium atom and the ring centroid-Al–Al angle is 170.1(3)°. The Al–Al bond length in **2** [2.591(3) Å] is shorter than those in the dialanes R_2AlAlR_2 [(R = $(Me_3Si)_2CH$ (2.660(1) Å)[14]; R = C_6H_2-2,4,6-Pr^i_3 C_6H_2 (2.647(3) Å)[15]; R = Bu^t_3 Si (2.751(2) Å)[16]], but identical to that in [RIAl–AlCl̇R] (R = $[(Me_3Si)_2C(Ph)C(Me_3Si)N]$) (2.593(2) Å)[17] within experimental error. As observed for **1**, there is considerable shortening of the Al–C distances of the $(\eta^5\text{-}Me_5C_5)Al$ monomer upon formation of the donor–acceptor bond. The sum of C–Al–C bond angles for the $Al(C_6F_5)_3$ moiety (333.0(3)°) is similar to that for the boron analogue **1**. The pronounced difference in the electronic environments of the donor and acceptor aluminium atoms in **2** is also evident from the disparity of ^{27}Al NMR chemical shifts (δ-115.7 and 106.9 for the Al(I) and Al(III) centres, respectively).



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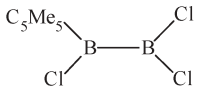

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The approach used for the synthesis of **2** was inappropriate for the preparation of a compound with a boron–boron donor–acceptor bond because of the unavailability of a boranediyl monomer or oligomer of empirical composition $(C_5Me_5)B$. However, Jutzi, Siebert *et al.*[18] discovered that the reaction of B_2Cl_4 with $(C_5Me_5)SiMe_3$ results in formation of the complex $(\eta^5\text{-}C_5Me_5)B$ → BCl_3 (**3**). It is likely that the first step of the reaction is Me_3SiCl elimination to form **4**, followed by a 1,2 chloride migration. At this juncture, it is interesting to note the parallel with the dialane to alanediyl-alane rearrangement that is also prompted by the introduction of a π-donating C_5Me_5 substituent.[11] A somewhat more complex exchange process accompanied the C_5Me_5 transfer reaction when decamethylsilocene, $(\eta^5\text{-}C_5Me_5)_2Si$, was treated with B_2Cl_4. Nevertheless, the isolated product $(\eta^5\text{-}C_5Me_5)B$ → BCl_2SiCl_3 (**5**)[18] also features a boron–boron donor–acceptor bond. Many of the aspects of the structures of **3** and **5** resemble those of **1** and **2**, particularly with respect to the virtual linearity of the B–B–X (ring centroid) vector and the pyramidal BCl_3 and BCl_2SiCl_3 moieties. An interesting nuance of these structures, however, is the slight bending of the C_5Me_5 methyl groups out of the C_5 ring plane and towards the univalent boron atom. This effect has been explained on a theoretical basis[19] and is also a feature of the structure of *e.g.* the $(\eta^5\text{-}C_5Me_5)Al$ monomer.[7] Within experimental error, the boron–boron bond distances in **3** [1.681(3) Å)] and **5** [(1.686(7) Å] are identical and fall within the range observed for conventional two-centre, two-electron, boron–boron bonds. As might be anticipated, **3** and **5** exhibit distinct ^{11}B NMR resonances corresponding to the univalent and trivalent boron atoms. Moreover, for both complexes, it was possible to measure the $J(^{11}B\text{–}^{11}B)$ NMR coupling constant (121 ± 5 Hz for **3** and 125 ± 3 Hz for **5**).

Interestingly, the heavier congeneric complexes with homonuclear donor–acceptor bonds were reported prior to the disclosures of their lighter analogues with B → B and Al → Al bonds. The first Ga → Ga bonded species, $[Tp^{Bu^t_2}]Ga$ → GaI_3 (**6**) ($Tp^{Bu^t_2}$ = *tris*(3,5-di-*tert*-butylpyrazolyl)hydroborate), was formed as one of the products of the reaction of $[Tp^{Bu^t_2}]Na$ with "GaI"(Fig. 3).[20] Inferentially, the GaI_3 in **6** results from disproportionation of sonochemically-produced "GaI."[21] The Ga → Ga bond distance in **6** (2.506(3) Å) is similar to those in *e.g.* $[\{(Me_3Si)_2CH)_2\}_2Ga]_2$ (2.541(1) Å),[22] $[(C_6H_2\text{-}2,4,6\text{-}Pr^i_3)_2Ga]_2$ (2.515(3) Å)[23] and $[\{(CF_3)_3C_6H_2\}_2Ga]_2$ (2.479(1) Å)[24] that feature conventional covalent Ga–Ga bonds. The fact that the average Ga–N bond length of 2.05(2) Å is more akin to those of Ga(III) complexes is due to the development of formal positive charge at the univalent gallium center, *viz.* $[Tp^{Bu^t_2}]\overset{+}{Ga}$ → $\overset{-}{Ga}I_3$. Additionally, DFT calculations indicate that the gallium "lone pair" of the model tris(pyrazolyl)hydroborate-substituted gallanediyl, [Tp]Ga, possesses Ga–N antibonding character and that the decrease in Ga–N bond distances that accompanies [Tp]Ga → GaI_3 formation is associated with the relief of this antibonding interaction.[25]

Other examples of species with gallium-gallium donor–acceptor bonds have been published more recently.[26] Interestingly, while $(\eta^5\text{-}C_5Me_5)Ga$ is hexameric in the solid state, this cluster undergoes facile monomerization in solution and in the gas phase.[27] Accordingly, it is a useful donor molecule that undergoes reaction with $Ga(Bu^t)_3$, $(\eta^1\text{-}C_5Me_5)GaCl_2$, and $(\eta^1\text{-}C_5Me_5)GaI_2$ to form the corresponding donor–acceptor complexes $(\eta^5\text{-}C_5Me_5)Ga$ → $Ga(Bu^t)_3$ (**7**) $(\eta^5\text{-}C_5Me_5)Ga$ → $Ga(Cl)_2(\eta^1\text{-}C_5Me_5)$ (**8**), and $(\eta^5\text{-}C_5Me_5)Ga$ → $Ga(I)_2(\eta^1\text{-}C_5Me_5)$ (**9**), of which **8** and **9** were characterized by X-ray crystallography.[26] Curiously, **8** was also formed *via* the reaction of $(\eta^5\text{-}C_5Me_5)Ga$ with InCl. In this case, InCl served as the source of chloride ligands to generate the requisite acceptor, $(\eta^1\text{-}C_5Me_5)GaCl_2$. The Ga → Ga bond distances in **8** (2.4245(3) Å) and **9** (2.437(2) Å) are slightly shorter than that in

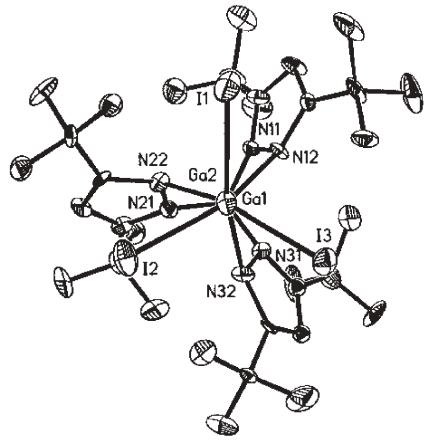


Fig. 3 View of the structure of $[Tp^{Bu^t_2}]Ga$ → GaI_3 (**6**) showing the atom numbering scheme.

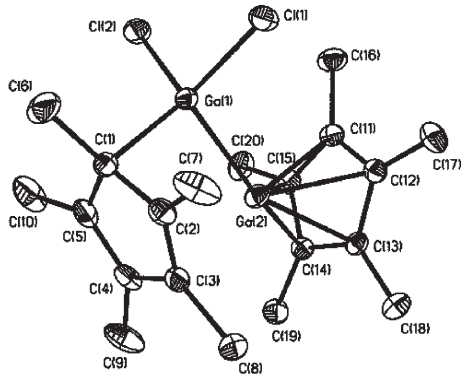


Fig. 4 View of the structure of (η^5-C_5Me_5)Ga → Ga(Cl)$_2$(η^1-C_5Me_5) (**8**) showing the atom numbering scheme.

the pyrazazolylborate complex **6** (2.506(3) Å). However, the most striking feature of the structures of **8** (Fig. 4) and **9** relate to their conformations. As noted above, in other donor–acceptor complexes, the ring centroid-element-element vector is essentially linear. However, in **8** and **9** the deviation from linearity is ~ 46°. In turn, the distances from the univalent gallium to the η^1-attached C_5Me_5 ring on the trivalent gallium atom are shorter than the sum of the van der Waals radii for gallium and sp^2-hybridized carbon atoms (3.6 Å). Further evidence for this interaction stems from the fact that the η^5-C_5Me_5 and η^1-C_5Me_5 rings cannot be distinguished on the NMR time scale down to −80 °C due to the rapid interchange of hapticities in solution.

Thus far, the sole example of a compound with an indium–indium donor–acceptor bond is [In_2I_3{η^3-HB(3-Bu^{t}pz)$_2$}-(5-Bu^{t}pz(η^1-5-Bu^{t}pzH)] (**10**).[28] This compound was prepared *via* the reaction of KHB(3-Bu^{t}pz)$_3$ with InI_3. Clearly, the [HB(3-Bu^{t}pz)$_3$]$^-$ anion plays the dual role of reducing agent and indium(I) stabilizing ligand. These processes are then followed by complexation of unreacted InI_3 to form **10**. The overall structure of **10** (Fig. 5) is somewhat more elaborate than that of the analogous gallium complex, **6**, in that the univalent indium atom is five- rather than four-coordinate due to the ligation of a Bu^{t}pzH molecule that presumably was generated by breakdown of a [HB(3-Bu^{t}pz)$_3$]$^-$ anion. The In–In dative bond distance in **10** (2.748(4) Å is identical with that in the diindane (C_6F_5)$_2$In–In(C_6F_5)$_2$ (2.744(2) Å)[29] and the I–In–I bond angles in **10** are comparable to those in Ph_3P → InI_3,[30] suggesting that the pyrazolylborate-substituted indanediyl is of comparable donor strength to that of Ph_3P.

Heteronuclear dative bonds

This review began with a discussion of Al → B donor–acceptor complexes. Running the gamut from boron to thallium, a total of

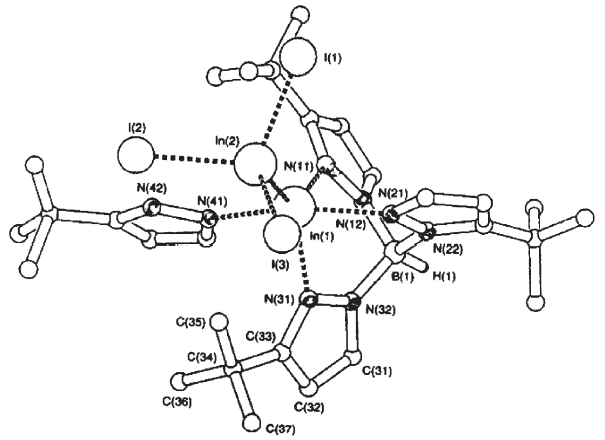


Fig. 5 View of the structure of [In_2I_3{η^3-HB(3-Bu^{t}pz)$_2$}(5-Bu^{t}pz(η^1-5-Bu^{t}pzH)] (**10**).

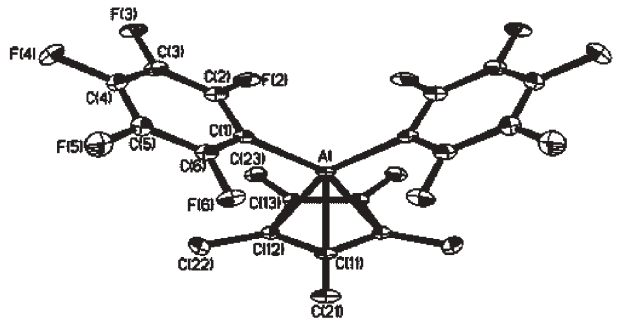


Fig. 6 View of the structure of (C_6F_5)$_2$Al(η^5-C_5Me_5) (**11**).

19 other complexes with heteronuclear group 13–group 13 donor–acceptor bonds can be anticipated. So far, only a handful of these possibilities have been realized. In terms of the alanediyl donor, (η^5-C_5Me_5)Al, it has not yet been possible to prepare complexes with Al → Ga or Al → In bonds. For example, when [Al(η^5-C_5Me_5)]$_4$ was treated with In(C_6F_5)$_3$[31] using the same procedure as that employed for the synthesis of **1**, the product was the Al(III) derivative, (C_6F_5)$_2$Al(η^3-C_5Me_5) **11** (Fig. 6).[3] By means of X-ray crystallography, it was established that the C_5Me_5 group of **11** is attached to aluminium in an η^3 fashion. This coordination mode is unusual and has been reported only for the chloride-bridged dimers, [(η^3-C_5Me_5)(R)(Al-μ-Cl]$_2$ (R = Me, Pr^i).[32] It is conceivable that **11** is produced *via* C_6F_5 group transfer from indium to aluminium of the initially formed complex, (η^5-C_5Me_5)Al → In(C_6F_5)$_3$, the other decomposition product being [In(C_6F_5)]$_x$. Such a view is consistent with the disparity in the M(I)/M(III) oxidation potentials for aluminium and indium as well as the relatively modest In–C bond energy.

It is evident from the discussion thus far that the η^5-C_5Me_5 ligand is very effective for the stabilization of group 13 elements in the univalent state.[33] More recent studies have revealed that β-diketiminate ligands are also very useful in this context.[34] For example, the gallanediyl HC[MeC(C_6H_3-2,6-Pr$^i_2$)N]$_2$Ga[35] is monomeric in the solid state while, as pointed out above, (η^5-C_5Me_5)Ga is monomeric in solution and hexameric in the solid state. Treatment of these bases with B(C_6F_5)$_3$ resulted in the first compounds with gallium–boron donor acceptor bonds, namely HC[MeC(C_6H_3-2,6-Pr$^i_2$)N]$_2$Ga → B(C_6F_5)$_3$ (**12**)[36] and (η^5-C_5Me_5)Ga → B(C_6F_5)$_3$ (**13**).[36,37] Analogously, the reaction of (η^5-C_5Me_5)Ga with Al(C_6F_5)$_3$ afforded (η^5-C_5Me_5)Ga → Al(C_6F_5)$_3$ (**14**) the first example of a compound with a gallium–aluminium donor–acceptor bond.[38] The gallium–boron distances are similar in **12** (2.156(1) ÅÅ) and **13** (2.160(2) Å) and slightly longer than that predicted for a single bond on the basis of the sum of covalent radii for Ga and B (2.10 Å), but fall within the range of Ga–B distances reported for a variety of gallium-substituted carboranes (2.14–2.33 Å).[39] Many of the aspects of the structure of **13** are analogous to those of **1**; for example, the ring centroid-Ga–B moiety is essentially linear and the average Ga–C distance is considerably shorter than those reported for (η^5-C_5Me_5)Ga (2.405(4) Å)[40] and [(η^5-C_5Me_5)Ga]$_6$ (2.380(9) Å.[6] In the β-diketiminate complex **12**, the C_3N_2Ga ring is essentially planar (Fig. 7) and the pattern of C–C and C–N distances is indicative of the delocalization of the π-electrons. The geometry at gallium is trigonal planar and the average Ga–N bond distance (1.942(6) Å) is shorter than that in the uncomplexed gallanediyl (av. 2.054(2) Å).[35] As explained in the case of **1**, such a shortening is expected to take place when the gallium lone pair is transformed into a gallium–boron dative bond with the concomitant development of formal positive and negative charges on the gallium and boron atoms, respectively. It is also possible that there is a decrease in the partial antibonding character of the Ga–N bonds as this transformation takes place. More recently, it has been found[41] that the monomeric (in solution) terphenyl-substituted gallanediyls (C_6H_3-2,6-Trip$_2$)Ga

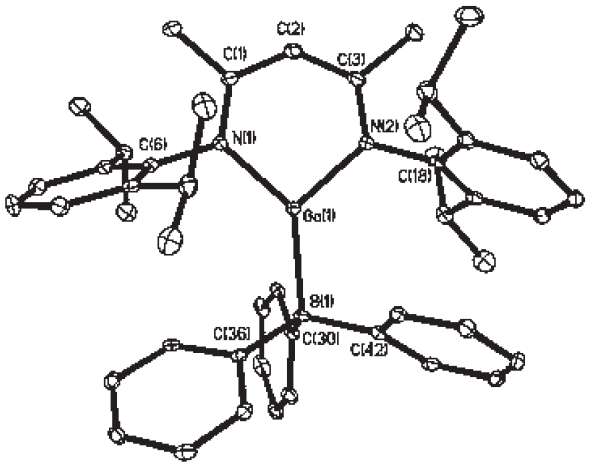


Fig. 7 View of the structure of $HC[MeC(2,6\text{-}Pr^i_2C_6H_3)N]_2Ga \rightarrow B(C_6F_5)_3$ (**12**) showing the atom numbering scheme.

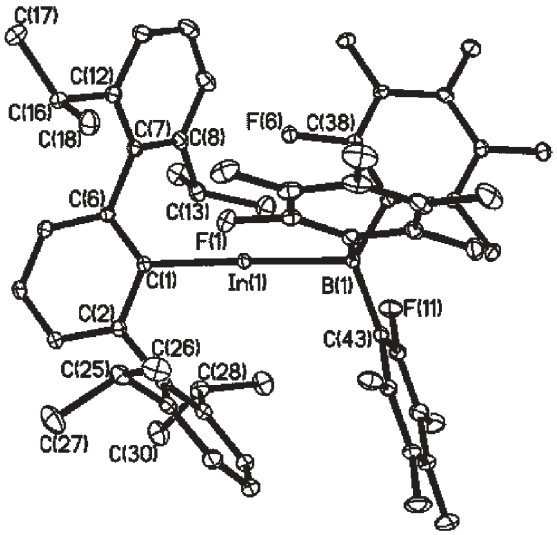


Fig. 8 View of the structure of $(C_6H_3\text{-}2,6\text{-}Dipp_2)In \rightarrow B(C_6F_5)_3$ (**17**) showing the atom numbering scheme.

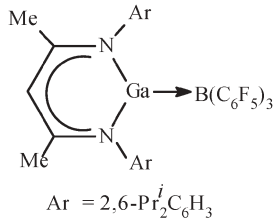
(Trip = C_6H_2-2,4,6-Pr^i_3), [C_6H_3-2,6-(Bu^tDipp)$_2$]Ga (Bu^tDipp = C_6H_2-2,6-Pr^i_2-4-Bu^t), and (C_6H_3-2,6-Dipp$_2$)Ga (Dipp = C_6H_3-2,6-Pr^i_2) react readily with $B(C_6F_5)_3$ to form (C_6H_3-2,6-Trip$_2$)Ga $\rightarrow$ $B(C_6F_5)_3$ (**15**), [C_6H_3-2,6-(Bu^tDipp)$_2$]Ga $\rightarrow$ $B(C_6F_5)_3$ (**16**), and (C_6H_3-2,6-Dipp)$_2$)Ga $\rightarrow$ $B(C_6F_5)_3$ (**17**), respectively. Each complex features an almost linearly coordinated gallium atom and the Ga $\rightarrow$ B bond lengths for **15** (2.110(3) Å), **16** (2.108(2) Å), and **17** (av. 2.124(6) Å) are shorter than those for **12** and **13**. This 0.03–0.04 Å shortening is presumably a consequence of the lower gallium coordination number in the terphenyl-substituted complexes.

Both examples of complexes with indium–boron dative bonds feature indanediyls with bulky terphenyl substituents. Interestingly, when the ligand C_6H_3-2,6-Dipp$_2$ (Dipp = C_6H_3-2,6-Pr^i_2) is employed, the indanediyl exists as a weakly-bound dimer in the solid state[42] while the use of the more highly substituted C_6H_2-2,4,6-Trip$_2$ ligand (Trip = C_6H_2-2,4,6-Pr^i_3) results in a stable monomer.[43] The reactions of these indanediyls with $B(C_6F_5)_3$ afforded the corresponding donor–acceptor complexes (C_6H_3-2,6-Dipp$_2$)In $\rightarrow$ $B(C_6F_5)_3$ (**18**)[42] (Fig. 8) and (C_6H_3-2,6-Trip$_2$)In $\rightarrow$ $B(C_6F_5)_3$ (**19**).[42] The In $\rightarrow$ B bond distances in **18** and **19** are 2.298(2) Å (av.) and 2.322(2) Å, respectively. The slightly longer In $\rightarrow$ B bond in **19** is probably due to the steric influence of the *para*-Pr^i groups. These distances compare with the sum of covalent radii for In and B (2.2 Å) and the range of In–B bond distances reported for cage compounds containing this moiety (2.25–2.52 Å).[44] Even though the indium atoms in **18** and **19** are two-coordinate, some close contacts with *ortho* fluorines were apparent. As expected on the basis of the increase of $In^{\delta+}$–$C^{\delta-}$ polarity, the In–C bond distances are shorter in **18** and **19** than in the corresponding indanediyls.

Relative basicities of group 13 diyls

Now that a few complexes with group 13 donor–acceptor bonds have been isolated and characterized, the question of the relative basicities of the group 13 diyl donors arises. One approach that has been proposed for such Lewis basicity determination is to measure the extent of departure from trigonal planarity of the BC_3 skeleton of $B(C_6F_5)_3$ when the donor–acceptor bond is formed, *i.e.* the sum of the three C–B–C bond angles.[45] The relevant data for the complexes of concern here are assembled in Table 1. Although the data are sparse, some preliminary observations can be made. On the basis of C–B–C bond angles the order of Lewis basicity is $HC(CMe)_2(NAr)_2Ga$ > (C_6H_3-2,6-Trip$_2$)Ga > (C_6H_3-2,6-Dipp$_2$)Ga > (C_6H_3-2,6-Trip$_2$)In > (C_6H_3-2,6-Dipp$_2$)In > (η^5-C_5Me_5)Al > [C_6H_3-2,6- (Bu^tDipp)$_2$]Ga > (η^5-C_5Me_5)Ga (Ar = Dipp = C_6H_3-Pr^i_2; Trip = C_6H_2-2,4,6-Pr^i_3; Bu^tDipp = C_6H_2-2,

Table 1 Bond angle (°) and bond distance (Å) data for $B(C_6F_5)_3$ complexes

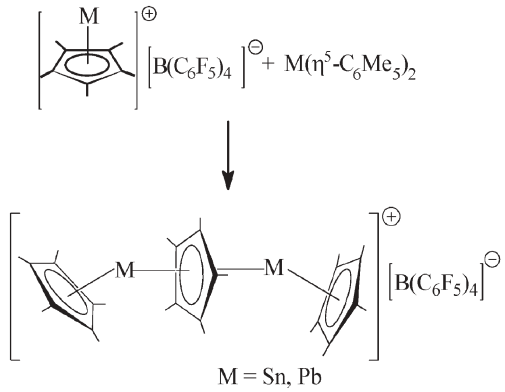
Complex	Sum of C–B–C bond angles	Element–Boron Distance	Reference
(η^5-C_5Me_5)Al $\rightarrow$ $B(C_6F_5)_3$ (**1**)	339.8(2)	2.169(3)	3
(η^5-C_5Me_5)Ga $\rightarrow$ $B(C_6F_5)_3$ (**13**)	342.2(2)	2.160(2)	36,37
	333.5(2) (av.)	2.149(3)	36
(C_6H_3-2,6-Trip$_2$)Ga $\rightarrow$ $B(C_6F_5)_3$ (**15**) (Trip = C_6H_2-2,4,6-Pr^i_3)	337.1(1)	2.110(3)	41
[C_6H_3-2,6-(Bu^tDipp)$_2$]Ga $\rightarrow$ $B(C_6F_5)_3$ (**16**) (Bu^tDipp = C_6H_2-2,6-Pr^i_2-4-Bu^t	340.0(3)	2.108(2)	41
(C_6H_3-2,6-Dipp$_2$)Ga $\rightarrow$ $B(C_6F_5)_3$ (**17**) (Dipp = C_6H_3-2,6-Pr^i_2)	337.5(3) (av.)	2.124(6) (av.)	41
(C_6H_3-2,6-Dipp$_2$)In $\rightarrow$ $B(C_6F_5)_3$ (**18**) (Dipp = C_6H_3-2,6-Pr^i_2)	339.32 (av.)	2.299(2)	42
(C_6H_3-2,6-Trip$_2$)In $\rightarrow$ $B(C_6F_5)_3$ (**19**) (Trip = C_6H_2-2,4,6-Pr^i_3)	337.79	2.322(2)	42
$(C_6H_5)_3P \rightarrow B(C_6F_5)_3$	339.9(4)	2.180(6)	45

6-Pr^i_2-4-Bu^t). In comparing the Me_5C_5-substituted diyls, note that (η^5-C_5Me_5)Al would appear to be a slightly stronger base than (η^5-C_5Me_5)Ga. This order is consistent with the general trend that basicity decreases upon descending a group of the Periodic Table. More surprising is the fact that the sum of C–B–C bond angles for the aluminanediyl complex **1** is almost identical to that for $(C_6H_5)_3PB(C_6F_5)_3$, thus implying that (η^5-C_5Me_5)Al and $(C_6H_5)_3P$ are of comparable donor strength. On the basis of the C–B–C bond angle criterion, the strongest Lewis base is the β-diketiminate-substituted gallanediyl, $HC[MeC(2,6\text{-}Pr^i_2C_6H_3)N]_2Ga$. The implication that the latter is a stronger donor than the other gallanediyls may be due to the accumulation of additional electron density on the lone pair of the β-dekiminate because of conjugative interaction from the nitrogen lone pairs. Note also that the gallium–boron distance in **12** is considerably shorter than that in **13**. The terphenyl-substituted gallanediyl and indanediyl complexes **15–19** have similar C–B–C angle sums to that of **1**, leading to the implication that the corresponding diyls and (η^5-C_5Me_5)Al are of comparable Lewis basicity. However, some caution should be exercised in over-interpreting these results. For example, element–boron bond distances and steric effects are likely to play an important role in the determination of Lewis basicity. Indeed, the fact that the C–B–C angle sum is slightly greater for **18** than for **19** may be due to the steric influence of the *para*-Pr^i substituents in the latter. Moreover, the fact that in **15–17** one C–B–C angle is more acute than the other two has been attributed to steric effects.[41] In future, it will be important to put the determination of diyl basicity on a firmer footing by conducting base competition studies and theoretical calculations.

The triple decker main group cation connection

When an attempt was made to extend the donor–acceptor chemistry to group 14 Lewis bases by treating $(\eta^5\text{-}C_5Me_5)_2Sn$ with $Ga(C_6F_5)_3$, somewhat surprisingly the product turned out to be the $[Ga(C_6F_5)_4]^-$ salt of the triple-decker cation $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^5\text{-}C_5Me_5)Sn(\eta^5\text{-}C_5Me_5)]^+$ (**20**) rather than the anticipated complex $(\eta^5\text{-}C_5Me_5)_2Sn \rightarrow Ga(C_6F_5)_3$.[46] Compound **20** is evidently the first example of a triple decker main group cation. However, two triple-decker main group anions, $[(\eta^5\text{-}C_5H_5)_3Tl_2]^-$ (**21**) and $[(\eta^5\text{-}(C_5H_5)_3Cs_2]^-$ (**22**), have been reported in the literature.[47,48] Although not proved, the most plausible route to **20** is the initial abstraction of a $[C_5Me_5]^-$ anion from $(\eta^5\text{-}C_5Me_5)_2Sn$ by the strong Lewis acid $Ga(C_6F_5)_3$ to form $[C_5Me_5Sn]^+$ and $[Ga(C_6F_5)_3(C_5Me_5)]^-$, the latter of which undergoes redistribution reactions to form $[Ga(C_6F_5)_4]^-$. The triple-decker cation is presumably formed by electrophilic attack of $[C_5Me_5Sn]^+$ on $(\eta^5\text{-}C_5Me_5)_2Sn$. Confirming this idea, it has been found subsequently that $[(\eta^5\text{-}C_5Me_5)M][B(C_6F_5)_4]$ salts (M = Sn, Pb) react with the corresponding decamethylmetallocenes $(\eta^5\text{-}C_5Me_5)_2M$ to form **20** and the lead triple-decker sandwich cation, $[(\eta^5\text{-}C_5Me_5)Pb(\mu\text{-}\eta^5\text{-}C_5Me_5)Pb(\eta^5\text{-}C_5Me_5)]^+$ (**23**)[49] as their $[B(C_6F_5)_4]^-$ salts (Scheme 1). It is clear from the X-ray crystal structure of [**20**][$Ga(C_6F_5)_4$] (Fig. 9) that the cation and anion are of comparable size, thus permitting optimization of the lattice energy. In this context, it is interesting to note that the reaction of stannocene with BF_3 does not result in a triple-decker system.[50] Instead, the solid state comprises a loose association of $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[(\eta^5\text{-}C_5Me_5)Sn]^+$ and THF units.

In the structure of **20**, a pentahapto C_5Me_5 ring serves as a bridging group for two $Sn(\eta^5\text{-}C_5Me_5)$ units. Within experimental error, the two Sn atoms are located equidistantly from the centroid of the bridging C_5Me_5 moiety and the average distance from each tin atom to this centroid (2.644(19) Å) is longer than that to the centroids of the terminal C_5Me_5 rings (2.246(18) Å). The average angle subtended at the tin centres (153.2(7)°) is very similar to that found for $Sn(\eta^5\text{-}C_5Me_5)_2$ (av. 154.9°).[51] Possibly the most intriguing aspect of the structures of **20** and **23** is the adoption of overall *cis*-type geometries in contrast to the triple decker anions



Scheme 1 Proposed mechanism for the formation of triple-decker cations **20** and **23**.

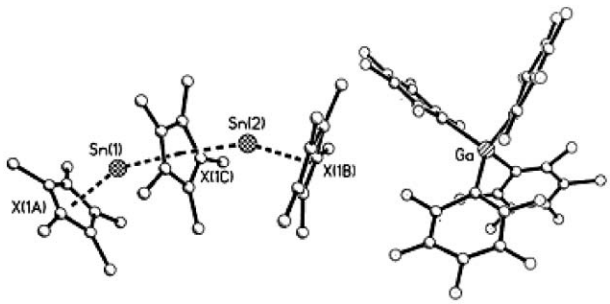
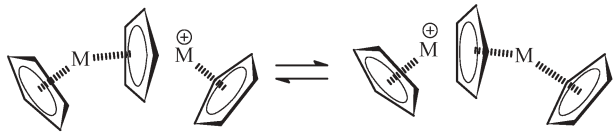


Fig. 9 View of the structure of $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^5\text{-}C_5Me_5)Sn(\eta^5\text{-}C_5Me_5)][Ga(C_6F_5)_4]$, [**20**][$Ga(C_6F_5)_4$].

21 and **22**, both of which possess transoid arrangements. The reason for this difference is not clear at the present time.

The triple-decker cations **20** and **23** are both stereochemically non-rigid in solution as evidenced by the detection of only one type of C_5Me_5 group in the ^1H and ^{13}C NMR spectra down to −100 °C. The dynamic process proposed in Scheme 2 is consistent with the fact that the Sn or Pb atoms are closer to the terminal C_5Me_5 rings than to the bridging C_5Me_5 ring. This facile exchange process also explains our lack of success in synthesizing triple decker cations with different metals.[49]

The first example of a group 13 triple-decker cation[46] was prepared *via* the reaction of $[(\eta^5\text{-}C_5Me_5)In]_6$[52] with an equimolar mixture of $B(C_6F_5)_3$ and the Brønsted acid $H_2O{\cdot}B(C_6F_5)_3$[53] in toluene solution. The idea was to generate $[In(arene)]^+$ cations by protolytic cleavage of the $In(\eta^5\text{-}C_5Me_5)$ monomer which, in turn, would attack unreacted $In(\eta^5\text{-}C_5Me_5)$ to form $[(\eta^6\text{-}C_7H_8)In(\mu\text{-}\eta^5\text{-}C_5Me_5)In(\eta^6\text{-}C_7H_8)]^+$ (**24**). The gegenion $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ was formed by deprotonation of $H_2O{\cdot}B(C_6F_5)_3$ followed by coordination to $B(C_6F_5)_3$. The overall geometry of **24** is *cis* as in the case of the group 14 triple decker cations. However, the pattern of bond distances in **24** is quite different from those in **20** and **23** in the sense that the distances from the indium atoms to the centroid of the bridging C_5Me_5 group (av. 2.481(4) Å) are considerably shorter than the indium–toluene ring centroids (av. 3.407(4) Å). The indium–toluene bonding is obviously extremely weak. In fact, MO calculations on the model system $[(\eta^6\text{-}C_6H_6)In(\mu\text{-}\eta^5\text{-}C_5H_5)In(\eta^6\text{-}C_6H_6)]^+$ indicate that the In–arene binding energy is only 6.6 kcal mol^{-1}.[46] Accordingly, **24** could



Scheme 2 Proposed mechanism for the fluxional behaviour of triple-decker cations **20** and **23**.

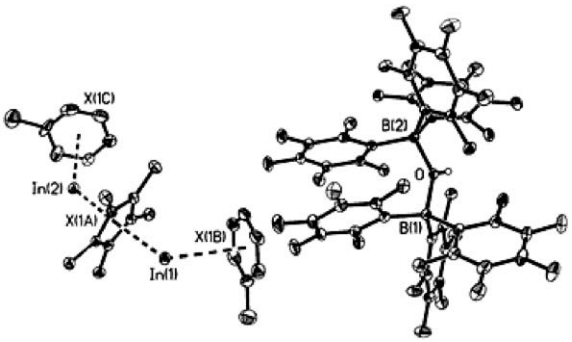


Fig. 10 View of the structure of $[(\eta^6\text{-}C_7H_8)In(\mu\text{-}\eta^5\text{-}C_5Me_5)In(\eta^6\text{-}C_7H_8)][(C_6F_5)_3BO(H)B(C_6F_5)_3]$, [**24**][$(C_6F_5)_3BO(H)(C_6F_5)_3$].

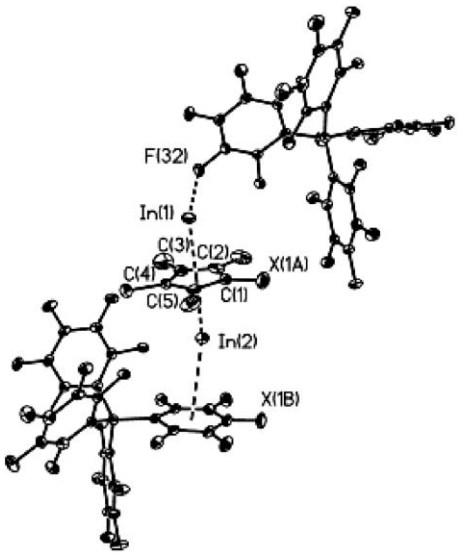


Fig. 11 View of the structure of $[In(\eta^5\text{-}C_5Me_5)In][B(C_6F_5)_4]$ (**25**).

be construed as the first example of an "inverse sandwich" main-group cation. Recognizing that the $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ anion is significantly larger than the cation **24** (Fig. 10), it was decided to replace it by a less voluminous anion. It was found[54] that treatment of two equivalents of $In(\eta^5\text{-}C_5Me_5)$ with one equivalent of the Brønsted acid [(toluene)H][$B(C_6F_5)_4$][49] in toluene solution results in the formation of $[In(\eta^5\text{-}C_5Me_5)In][B(C_6F_5)_4]$ (**25**) (Fig. 11). NMR spectroscopy provided no evidence for the presence of toluene in the cation structure, an indication that was confirmed by X-ray crystallography.

Concluding remarks

The existence of stable compounds with intra group 13 donor–acceptor bonding implies that boranediyls (RB) and heavier congeneric univalent species are reasonably strong Lewis bases. This donor property has permitted the isolation and structural assay of a number of compounds with unusual, and in some cases unprecedented, group 13–group 13 bonds. In the future, it will be very useful to have a more quantitative assessment of the relative basicities of the group 13 diyls from base competition studies in conjunction with theoretical modeling and spectroscopic measurements. If indeed the Lewis basicity of *e.g.* $(\eta^5\text{-}C_5Me_5)Al$ is comparable to that of $(C_6H_5)_3P$, this would herald its use in a much wider context than group 13 chemistry. In terms of the multi-decker cations, future work will focus both on the synthesis of triple-decker structures that are less labile in solution and also on the assembly of more highly aggregated multi-decker systems.

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